



## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of )

Fanny BARBOTIN et al. )

Application No.: 09/688,376 )

Filed: October 11, 2000 )

For: SOLID SUPPORTED CATALYST  
USABLE FOR THE  
POLYMERIZATION OF  
CONJUGATED DIENES,  
PROCESS FOR THE  
PREPARATION THEREOF AND  
A PROCESS FOR THE  
POLYMERIZATION OF  
CONJUGATED DIENES USING  
THIS CATALYST )

Group Art Unit: 1755

Examiner: James W. Pasterczyk

Appeal No.:

Confirmation No.: 5867

## BRIEF FOR APPELLANT

## Mail Stop APPEAL BRIEF - PATENTS

Commissioner for Patents

P.O. Box 1450

Alexandria, VA 22313-1450

Sir:

This appeal is from the decision of the Primary Examiner dated March 26, 2004, finally rejecting claims 1-20 and 24, which are reproduced as an Appendix to this brief.

A check covering the ☐ \$165.00 (2402) ☒ \$330.00 (1402) Government fee and two extra copies of this brief are being filed herewith.

The Commissioner is hereby authorized to charge any appropriate fees under 37 C.F.R. §§1.16, 1.17, and 1.21 that may be required by this paper, and to credit any overpayment, to Deposit Account No. 02-4800. A copy of this page and the signature page are submitted in triplicate.

I. Real Party in Interest

The present application is assigned to MICHELIN RECHERCHE ET  
TECHNIQUE S.A..

II. Related Appeals and Interferences

The Appellant's / Appellants' legal representative, or assignee, does not know of any other appeal or interferences which will affect or be directly affected by or have bearing on the Board's decision in the pending appeal.

III. Status of Claims

Claims 1-20 and 24 are currently pending in this application. Claims 21-23 have been canceled.

IV. Status of Amendments

The Amendment filed March 1, 2004, pursuant to 37 C.F.R. §1.116 has been entered.

V. Summary of the Invention

The claims on appeal are directed to a solid supported catalyst for the polymerization of dienes and methods of preparing the catalyst. The catalyst comprises a reaction product of (1) a solid support comprising an inorganic metal oxide compound such as silica, and (2) a complex represented by the formula  $M(Ar)(AlX_4)_3$  where M is a rare earth element having an atomic number between 57 and 71 such as neodymium, Ar is an aromatic hydrocarbon solvent such as toluene, and X is a halogen. Note page 3, lines 17-25 of the specification. The catalyst may also include a compound of the formula  $AlX_nR_{3-n}$  where X is halogen, R is hydrogen or an alkyl group of 1-15 carbon atoms, and n is 0 to 3. Note claim 9 and page 8, lines 3-9 of the specification.

The catalysts of the invention may be prepared by several different methods. In a first method, a complex of the formula  $M(Ar)(AlX_4)_3$  is prepared by reacting a

halide of the formula  $MX_3$  with an aluminum halide in an aromatic hydrocarbon solvent Ar, and reacting the complex with an inorganic oxide support. Preferably, the solid support is initially prepared by reacting an inorganic metal oxide with a Lewis acid of the formula  $M'X_n$  where X represents halogen, n is an integer of 3 to 5, and M' is boron, aluminum, titanium, iron, zirconium, tin, antimony, hafnium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium or lutetium. See pages 4-6 of the specification.

The catalysts of the invention may also be prepared by reacting an inorganic oxide support in an aromatic hydrocarbon solvent Ar with an aluminum halide of the formula  $AlX_3$ , and reacting the resultant product with a compound of the formula  $MX_3$  to form *in situ* the complex  $M(Ar)(AlX_4)_3$ . Note claim 12 and page 6 of the specification.

Still another method of preparing the claimed catalysts comprises simultaneously reacting an inorganic oxide support with an excess of an aluminum halide of the formula  $AlX_3$  and a metal halide of the formula  $MX_3$  in the presence of an aromatic hydrocarbon solvent Ar to prepare *in situ* a reaction product of a complex of the formula  $M(Ar)(AlX_4)_3$  and the inorganic oxide. Note claim 13 and page 7 of the specification.

In any of the above methods, the inorganic oxide can be pre-reacted with a Lewis acid of the formula  $M'X_3$  as described in claim 17. Also, the catalysts prepared by any of the above methods can be further reacted with a compound of the formula  $AlX_nR_{3-n}$  as described on page 8 and in claim 14.

Applicants have surprisingly discovered that the presently claimed catalysts when used in the polymerization of dienes, yield polymers having higher viscosities and higher content of cis-1,4 linkages than expected based on prior art disclosures. Note the working examples in the specification.

## VI. The Issues

The sole issue raised on appeal is as follows: whether claims 1-20 and 24 were properly rejected under 35 U.S.C. §103(a) as obvious over the article by Hu et

al. appearing in the Chinese Science Bulletin (Vol. 37, April 1992, pages 566-570) in view of WO 92/17510 to Jones et al.

## VII. Grouping of Claims

For purposes of this appeal, claims 1-6, 9-11, 14 (9), 14 (10), 14 (11) and 24 stand or fall together.

Claims 7, 8 and 17-20 are separately patentable and stand or fall together.

Claims 12, 13, 14 (12) and 14 (13) are separately patentable and stand or fall together.

## VIII. Argument

In the Final Rejection mailed November 14, 2003, claims 9, 12, 13, 15 and 24 were rejected under 35 U.S.C. §112, second paragraph, for the reasons given in paragraph (2) of the Office Action. An Amendment pursuant to 37 C.F.R. §1.116 was filed March 1, 2004. The Advisory Action mailed March 26, 2004, indicated that the Amendment filed March 1, 2004, would be entered for appeal purposes and would obviate the rejection under 35 U.S.C. §112, second paragraph.

With respect to the §103(a) rejection, the Examiner's position is that it would have been obvious to one of ordinary skill in the art at the time of the present invention to modify the catalyst disclosed in Hu et al. by supporting the catalyst on an inorganic oxide in view of the disclosure in WO '510. Respectfully, Appellants disagree for at least the reasons which follow.

The Hu et al. article discloses that the homogeneous complex  $\text{NdC}_6\text{H}_5(\text{AlCl}_4)_3\text{-AlR}_3$  can be used to initiate the cis-1,4 stereospecific polymerization of isoprene. The unpredictability of catalyst behavior is emphasized by the data in Table 2 on page 568 of the article. The data shows that tri-isobutyl aluminum and diisobutyl aluminum hydride improve catalytic activity while triethyl aluminum and trioctyl aluminum have no effect on catalyst activity. The Hu et al. article does not disclose or suggest that the homogeneous catalyst can be reacted with an inorganic oxide solid support.

WO '510 (Jones et al) is directed to the polymerization of olefins using pi-arene complexes of lanthanide metals. The complexes can be reacted with inorganic oxide solid supports. Preferred olefin monomers are 1-monoolefins such as ethylene and propylene. Copolymers of ethylene and/or propylene with "a diene such as butadiene" are mentioned on page 7, lines 7-9 of this document. The 28 working examples of WO '510 are all directed to homopolymerization of ethylene or propylene. The reference teaches that the supported complexes are less reactive than the complexes per se (page 6, lines 34-35) and that the presence of co-catalysts and activators can be tolerated "although usually incurring some loss of activity" (page 7, lines 17-19).

To establish a *prima facie* case of obviousness, the prior art relied upon, coupled with the knowledge generally available in the art at the time of the invention, must contain some suggestion or incentive that would have motivated the skilled artisan to modify a reference or to combine references. See Karsten Mfg. Corp. v. Cleveland Gulf Co., 242 F.3d 1376,1385, 58 U.S.P.Q.2d 1286,1293 (Fed. Cir. 2001) ("In holding an invention obvious in view of a combination of references, there must be some suggestion, motivation, or teaching in the prior art that would have led a person of ordinary skill in the art to select references and combine them in the way that would produce the claimed invention."); C.R. Bard, Inc. v. M3 Sys., Inc. 157 F.3d 1240,1352, 48 U.S.P.Q.2d 1225,1232 (Fed. Cir. 1998) (a showing of a suggestion, teaching, or motivation to combine the prior art references is an "essential evidentiary component of an obviousness holding"). Northern Telecom v. Datapoint Corp., 908 F.2d 931,934, 15 U.S.P.Q.2d 1321,1323 (Fed. Cir. 1990) ("It is insufficient that the prior art disclosed the components of the patented device, either separately or used in other combinations; there must be some teaching, suggestion, or incentive to make the combination made by the inventor."). The teachings or suggestions, as well as the second requirement, expectation of success, must come from the prior art, not applicant's disclosure. See In re Vaeck, 947 F.2d 488,493, 20 U.S.P.Q.2d 1438,1442 (Fed. Cir. 1991). The proposed modification of the prior art must have had a reasonable expectation of success, determined from the vantage

point of the skilled artisan at the time the invention was made. In other words, a hindsight analysis is not proper.

Appellants respectfully submit that the respective teachings of the references represent only isolated disclosures with no suggestion or incentive therein that would have motivated those of ordinary skill to modify their respective disclosures and arrive at the invention set forth in the present claims. Nor was there a reasonable expectation that modifying the catalyst disclosed in Hu et al. in accordance with the teachings in WO '510 would successfully polymerize isoprene to provide stereospecific polymers having high cis-1,4 contents and acceptable molecular weights.

It is the Appellants' position that those of ordinary skill in the art would not seek to enhance the activity of the isoprene catalysts of Hu et al. by looking in the direction of the 1-monoolefin catalysis of WO '510. Catalytic activity is notoriously unpredictable (In re Mercier, 185 USPQ 774: "The unpredictability of catalytic phenomena has long been recognized by this court"; pg. 779). Thus, those of ordinary skill in the art could not reasonably predict that the catalyst supports described in WO '510 primarily for 1-monoolefin polymerization could be used to improve the activity of the isoprene catalysts of Hu et al.

There is no disclosure or suggestion in Hu et al. that the catalytic complexes disclosed therein could be disposed on supports of any kind, let alone inorganic oxides. Although WO '510 does mention the possible use of butadiene as a comonomer (page 7, line 9), the 28 specific polymerization examples disclosed therein involve the homopolymerization of ethylene or propylene. Thus, when one reviews the entire disclosure of WO '510 as a whole, one must conclude that the teachings thereof are restricted to the polymerization of 1-monoolefins.

To further emphasize the unpredictable nature of determining the viability of transferring catalytic activity from one system to another, it should be noted from Table 1 of Hu et al. that one neodymium complex showed relatively high catalytic activity for isoprene polymerization while a similar neodymium complex showed no catalytic activity for isoprene. A review of the data in Table 2 of Hu et al. shows that neodymium complexes containing certain aluminum alkyls, i.e., Al(*i*-Bu)<sub>3</sub> and

$\text{Al}(\text{i-Bu})_2\text{H}$  exhibit catalytic activity while other Al trialkyls such as triethyl aluminum show no activity. It should be noted further that the presently claimed catalysts which contain triethyl aluminum do exhibit catalytic activity for conjugated diene polymerization.

Hu et al. disclose a homogeneous catalyst for polymerizing isoprene. As explained in the present specification, a disadvantage of the homogeneous catalyst of Hu et al. resides in undesirably low viscosity values and undesirably low cis-1,4 linkages in the resultant polyisoprene (present specification, page 3, lines 1-12). Polyisoprenes obtained using the catalyst disclosed by Hu et al. exhibit cis-1,4 linkages content of between 92.6% to 93.9% (see Hu et al., Tables 2-3) and a viscosity of 2.02 and 2.18 at 50°C and 30°C and only 0.73 at 70°C (see Hu et al. in Table 4).

In contrast, the conjugated diene obtained using the catalyst of the present invention exhibit cis-1,4 linkages content of between 96.1% to above 99% (present specification, Examples 1-12) and an inherent viscosity as high as 6.5 dl/g at 60°C (present specification, Example 5). The polyisoprenes prepared using the catalyst of the present invention have higher viscosities and cis-1,4 contents than those prepared by the catalyst disclosed in Hu et al. Note page 15 of the specification. Thus, the presently claimed catalysts clearly and unexpectedly performed better than the catalysts of Hu et al.

Furthermore, one of ordinary skill would not seek to combine the teachings of Hu et al. and WO '510 because the degree of oxidation of the earth metals is different. In WO '510, the pi-arene lanthanide complexes have a degree of oxidation equal to 0. When reacted with the support, the oxidation level is raised to 2 (page 4, line 30 to page 5, line 1). In Hu et al. and the present application, the level of oxidation of Nd for example, is 3. Nd does not exist at a level of oxidation of 5. Thus, contrary to the situation in WO '510, an increase in the level of oxidation of Nd by two is not possible. Accordingly, it would not have been obvious to those skilled in the art to apply the teachings of WO '510 to Hu et al.

It is clear from the above arguments that those of ordinary skill would not have been motivated to use the inorganic oxides disclosed in WO '510 as supports for the

catalytic complexes described in Hu et al. Due to the recognized difficulty in predicting catalytic activity, there would be no reasonable expectation that catalysts obtained by combining the teachings of the cited art would successfully polymerize conjugated diolefins. It is the present inventors who unexpectedly discovered that complexes of the type disclosed in Hu et al. when reacted with inorganic oxide supports, could be used to obtain conjugated diolefin polymers possessing significantly higher viscosities and contents of cis-1,4 linkages.

Claims 7, 8 and 17-20 are directed to a separate embodiment. These claims are directed to catalysts and processes of preparing catalysts wherein the inorganic oxide supports are reacted with a Lewis acid of the formula  $M'X_n$  either alone or in the presence of a metal halide of the formula  $MX_3$ . There is no disclosure in WO '510 to react the inorganic oxide supports with Lewis acids let alone in the manner set forth in claims 7, 8 and 17-20. As a matter of fact, WO '510 suggests that co-catalysts and activators should be avoided since they are prone to reduce catalytic activity.

Claims 12, 13, 14 (12) and 14 (13) are directed to processes of preparing the catalysts of the invention. WO '510 only discloses a process of preparing the catalysts by reacting the inorganic supports with the previously prepared pi-arene lanthanide complexes. There is no disclosure or suggestion in WO '510 of preparing the catalysts by the processes set forth in claims 12, 13, 14 (12) and 14 (13).

For at least the above reasons, Appellants submit that the §103(a) rejection based on the Hu et al. article combined with WO '510 does not establish a *prima facie* case of obviousness. Hu et al. does not suggest the use of inorganic oxide supports, the catalysts of Hu et al. and WO '510 are significantly different, WO '510 discourages the use of co-catalysts and activators. Only impermissible hindsight has been used to arrive at the presently claimed invention.



IX. Conclusion

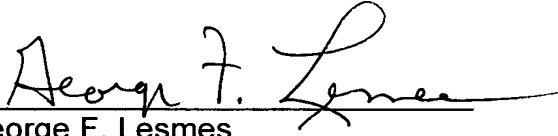
In view of the above arguments, Appellants respectfully submit that the §103(a) rejection of claims 1-20 and 24 is unsound and should be reversed. Such action is earnestly solicited.

Respectfully submitted,

Burns, Doane, Swecker & Mathis, L.L.P.

Date July 21, 2004

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## **APPENDIX A**

### **The Appealed Claims**

1. A solid supported catalyst for the polymerization of conjugated dienes, comprising a reaction product of
  - a. a complex represented by formula  $M(Ar)(AlX_4)_3$ , where M is selected from the group consisting of lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium, Ar is an aromatic hydrocarbon solvent, Al is aluminum and X is selected from the group consisting of fluorine, chlorine, bromine and iodine, and
  - b. a solid support comprising an inorganic metal oxide compound.
2. The solid supported catalyst according to Claim 1, wherein the solid support comprises silica.
3. The solid supported catalyst according to Claim 1 or 2, further comprising a compound represented by formula  $AlX_nR_{3-n}$ , where Al is an aluminum atom, X is selected from the group consisting of fluorine, chlorine, bromine and iodine, R is a hydrogen atom or an alkyl group having from 1 to 15 carbon atoms and n is an integer ranging from 0 to 3.

4. The solid supported catalyst according to Claim 3, wherein  $AlX_nR_{3-n}$  is triethylaluminum, triisobutylaluminum or diethylaluminum chloride.

5. The solid supported catalyst according to Claim 1 wherein M is neodymium.

6. The solid supported catalyst according to Claim 1 wherein X is chlorine.

7. The solid supported catalyst according to Claim 1 wherein the solid support comprises the reaction product of an inorganic metal oxide compound with a Lewis acid of the formula  $M'X_n$ , where n is an integer ranging from 3 to 5, X is selected from the group consisting of fluorine, chlorine, bromine and iodine and M' is selected from the group consisting of boron, aluminum, titanium, iron, zirconium, tin, antimony, hafnium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium.

8. The solid supported catalyst according to Claim 7 wherein M' is selected from the group consisting of boron, titanium, iron, aluminum, zirconium, tin, hafnium and antimony.

9. A process for the preparation of a solid supported catalyst comprising the reaction product of

a. a complex represented by formula  $M(Ar)(AlX_4)_3$ , where M is selected from the group consisting of lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium, Ar is an aromatic hydrocarbon solvent and X is selected from the group consisting of fluorine, chlorine, bromine and iodine, and

b. a solid support comprising an inorganic metal oxide compound, said process comprising

(i) preparing said solid support,

(ii) preparing said complex of formula  $M(Ar)AlX_4)_3$  by reacting, in solvent Ar, a halide of metal M, represented by the formula  $MX_3$ , and a halide of aluminum, represented by the formula  $AlX_3$ , wherein  $MX_3$  and  $AlX_3$  contain the same halogen X, and

(iii) reacting said complex with said solid support to obtain said catalyst.

10. The process according to Claim 9, wherein the molar ratio  $AlX_3:MX_3$  is greater than or equal to 3.

11. The process according to Claim 10, wherein the molar ratio is between 4 and 7.

12. A process for the preparation of a solid supported catalyst, comprising the reaction product of

a. a complex represented by formula  $M(Ar)(AlX_4)_3$ , where M is selected from the group consisting of lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium, Ar is an aromatic hydrocarbon solvent and X is selected from the group consisting of fluorine, chlorine, bromine and iodine, and

b. a solid support comprising an inorganic metal oxide compound, said process comprising

(i) reacting the solid support in the aromatic hydrocarbon solvent Ar with an excess of an aluminum halide represented by formula  $AlX_3$  and

(ii) reacting the product of (i) with a halide of the metal represented by the formula  $MX_3$ , wherein  $AlX_3$  and  $MX_3$  contain the same halogen X, in order to form the catalyst comprising complex  $M(Ar)(AlX_4)_3$ .

13. A process for the preparation of a solid supported catalyst comprising the reaction product of

- a. a complex represented by formula  $M(Ar)(AlX_4)_3$ , where M is selected from the group consisting of lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium, Ar is an aromatic hydrocarbon solvent and X is selected from the group consisting of fluorine, chlorine, bromine and iodine, and
- b. a solid support comprising an inorganic metal oxide compound, said process comprising concomitantly reacting, in the aromatic hydrocarbon solvent Ar, said solid support with an excess of aluminum halide  $AlX_3$ , and a metal halide of a metal represented by the formula  $MX_3$ , wherein  $AlX_3$  and  $MX_3$  contain the same halogen X, in order to form the catalyst comprising complex  $M(Ar)(AlX_4)_3$ .

14. The process according to any of Claims 9 to 13, further comprising reacting said catalyst with a compound represented by formula  $AlX_nR_{3-n}$ , where Al is an aluminum atom, X is selected from the group consisting of fluorine, chlorine, bromine and iodine, R is a hydrogen atom or an alkyl group having from 1 to 15 carbon atoms and n is an integer ranging from 0 to 3, inclusive.

15. The process according to Claim 14, wherein  $AlX_nR_{3-n}$  is triethylaluminum, triisobutylaluminum or diethylaluminum chloride.

16. The process according to any of Claims 9, 12 or 13, further comprising dehydrating said inorganic metal oxide compound and then partially dehydroxylating said compound by heat treatment at a temperature of between 300°C and 800°C.

17. The process according to any of Claim 9, 12 or 13, wherein the solid support comprises the reaction product of an inorganic metal oxide compound with a Lewis acid of the formula  $M'X_n$ , where  $n$  is an integer ranging from 3 to 5, inclusive,  $X$  is selected from the group consisting of fluorine, chlorine, bromine and iodine and  $M'$  is selected from the group consisting of boron, aluminum, titanium, iron, zirconium, tin, antimony, hafnium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium.

18. The process according to Claim 17, wherein said  $M'$  is selected from the group consisting of boron, titanium, iron, aluminum, zirconium, tin, hafnium and antimony.

19. The process according to Claim 17, further comprising reacting said Lewis acid of formula  $M'X_n$  in the solid state and in excess with said inorganic metal oxide compound and subliming said acid.



20. The process according to Claim 17, wherein said Lewis acid of formula  $M'X_n$  is reacted in solution in an inert hydrocarbon solvent with said inorganic metal oxide compound.

24. The solid supported catalyst according to Claim 3 wherein X in the formula  $AlX_nR_{3-n}$  is chlorine.